CHAPTER 11

NITROGEN OXIDES (NOx) CONTROL AND REDUCTION TECHNIQUES

11-1. Formation of nitrogen oxides.

a. Nitrogen oxides (NO_x). All fossil fuel burning processes produce NO_x. The principle oxides formed are nitric oxide (NO) which represents 90-95 percent (%) of the NO_x formed and nitrogen dioxide (NO_2) which represents most of the remaining nitrogen oxides.

b. NO_x formation. Nitrogen oxides are formed primarily in the high temperature zone of a furnace where sufficient concentrations of nitrogen and oxygen are present. Fuel nitrogen and nitrogen contained in the combustion air both play a role in the formation of NO_x. The largest percentage of NO_x formed is a result of the high temperature fixation reaction of atmospheric nitrogen and oxygen in the primary combustion zone.

c. NO_x concentration. The concentration of NO_x found in stack gas is dependent upon the time, temperature, and concentration history of the combustion gas as it moves through the furnace. NO_x concentration will increase with temperature, the availability of oxygen, and the time the oxygen and nitrogen simultaneously are exposed to peak flame temperatures.

11-2. Factors affecting NO_x emissions

a. Furnace design and firing type. The size and design of boiler furnaces have a major effect on NO_x emissions. As furnace size and heat release rates increase, NO_x emissions increase. This results from a lower furnace surface-to-volume ratio which leads to a higher furnace temperature and less rapid terminal quenching of the combustion process. Boilers generate different amounts of NO_x according to the type of firming. Units employing less rapid and intense burning from incomplete mixing of fuel and combustion gases generate lower levels of NO_x emissions. Tangentially fired units generate the least NO_x because they operate on low levels of excess air, and because bulk misting and burning of the fuel takes place in a large portion of the furnace. Since the entire furnace acts as a burner; precise proportioning of fuel/air at each of the individual fuel admission points is not required. A large amount of internal recirculation of bulk gas, coupled with slower mixing of fuel and air, provides a combustion system which is inherently low in NO_x production for all fuel types.

b. Burner design and configuration. Burners operating under highly turbulent and intense flame conditions produce more NO_x. The more bulk mixing of fuel and air in the primary combustion zone, the more turbulence is created. Flame color is an index of flame turbulence. Yellow hazy flames have low turbulence, whereas, blue flames with good definition are considered highly turbulent.

c. Burner number. The number of burners and their spacing are important in NO_x emission. Interaction between closely spaced burners, especially in the center of a multiple burner installation, increases flame temperature at these locations. The tighter spacing lowers the ability to radiate to cooling surfaces, and greater is the tendency toward increased NO_x emissions.

d. Excess air. A level of excess air greatly exceeding the theoretical excess air requirement is the major cause of high NO_x emissions in conventional boilers. Negotiable quantities of thermally formed NO_x are generated in fluidized bed boilers.

e. Combustion temperature. NO_x formation is dependent upon peak combustion temperature, with higher temperatures producing higher NO_x emissions.

f. Firing and quenching rates. A high heat release rate (firing rate) is associated with higher peak temperatures and increased NO_x emissions. A high rate of thermal quenching, (the efficient removal of the heat released in combustion) tends to lower peak temperatures and contribute to reduced NO_x emissions.

g. Mass transportation and mixing. The concentration of nitrogen and oxygen in the combustion zone affects NO_x formation. Any means of decreasing the concentration such as dilution by exhaust gases, slow diffusion of fuel and air; or alternate fuel-rich/fuel- lean burner operation will reduce NO_x formation. These methods are also effective in reducing peak flame temperatures.

h. Fuel type. Fuel type affects NO_x formation both through the theoretical flame temperature reached, and through the rate of radiative heat transfer. For most combustion installations, coal-fired furnaces have the highest level of NO_x emissions and gas-fired installations have the lowest levels of NO_x emissions.

i. Fuel nitrogen. The importance of chemically bound fuel nitrogen in NO_x formation varies with the temperature level of the combustion processes. Fuel nitrogen is important at low temperature combustion, but its contribution is nearly negligible as higher flame temperatures are reached, because atmospheric nitrogen contributes more to NO_x formation at higher temperatures.

11-3. NO_x reduction techniques

a. Fuel selection. Reduction of NO_x emissions may be accomplished by changing to a fuel which decreases the combustion excess air requirements, peak flame temperatures, and nitrogen content of the fuel. These changes decrease the concentration of oxygen and nitrogen in the flame envelope and the rate of the NO_x formation reaction.

(1) The specific boiler manufacturer should be consulted to determine if a fuel conversion can be performed without adverse effects. The general NO_x reduction capability of initiating a change in fuel can be seen comparatively in table 11-1.

(2) A consideration when comtemplating a change in fuel type is that NO_x emission regulations are usually based on fuel type. Switching to a cleaner fuel may result in the necessity of conforming to a more strict emission standard.

Table 11–1

General NO_x emission and excess air requirements for fuel types

Fuel Type	Range of Excess Air Level, percent above stoichiometric	NO_x Emissions lbs/Mil Btu
Coal	18–25	.5–1.1
(Lignite)	–	(.9–1.1)
Fuel Oil	3–15	.1– .4
Gaseous fuels	7–10	.3

(3) Changing from a higher to a lower NO_x producing fuel is not usually an economical method of reducing NO_x emissions because additional fuel costs and equipment capital costs will result. For additional information on fuel substitution, see paragraph 10-3. In doing so, it should be noted that changing from coal to oil or gas firing is not in accordance with present AR 420-49.

b. Load reduction. Load reduction is an effective technique for reducing NO_x emissions. Load reduction has the effect of decreasing the heat release rate and reducing furnace temperature. A lowering of furnace temperature decreases the rate of NO_x formation.

(1) NO_x reduction by load reduction is illustrated in figure 11-1. As shown, a greater reduction

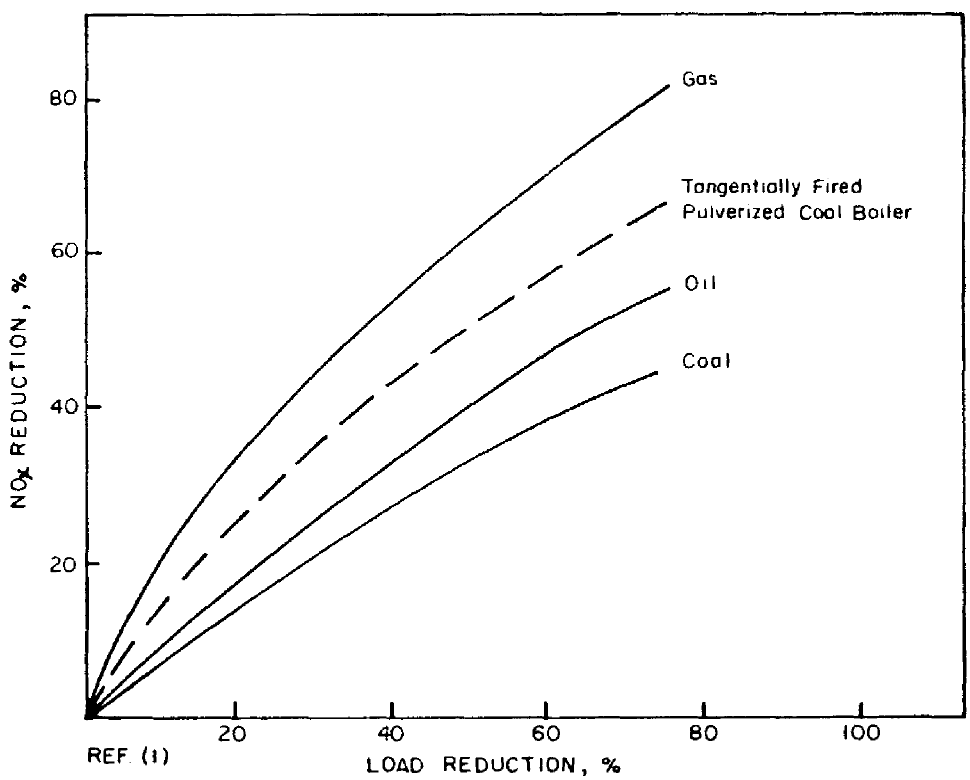

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Figure 11–1. Possible NO_x reductions vs load reductions in NO_2 is attainable burning gas fuels because they contain only a small amount of fuel-bound nitrogen. Fuel-bound nitrogen conversion does not appear to be affected by furnace temperatures, which accounts for the lower NO_x reductions obtained with coal and oil firing. Some units such as tangentially fired boilers show as much as 25 percent decrease in NO_x emissions with a 25 percent load reduction while burning pulverized coal.

(2) Although no capital costs are involved in load reduction, it is sometimes undesirable to reduce load because it may reduce steam cycle efficiency.

c. Low excess air firing (LEA). In order to complete the combustion of a fuel, a certain amount of excess air is necessary beyond the stoichiometric requirements. The more efficient the burners are in misting, the smaller will be the excess air requirement. A minimum amount of excess air is needed in any system to limit the production of smoke or unburned combustibles; but larger amounts may be needed to maintain steam temperature to prevent refractory damage; to complete combustion when air supply between burners is unbalanced; and to compensate for instrument lag between operational changes. Practical minimums of excess air are 7 percent for natural gas, 3 to 15 percent for oil firing, and 18 to 25 percent for coal firing.

(1) Since an increase in the amount of oxygen and nitrogen in a combustion process will increase the formation and concentration of NO_x, low excess air operation is the first and most important technique that should be utilized to reduce NO_x emissions. A 50 percent reduction in excess air can usualy reduce NO_x emissions from 15 to 40 percent, depending upon the level of excess air normally applied. Average NO_x reductions corresponding to a 50 percent reduction in excess air for each of the three fuels in different boiler types are shown in table 11-2. Reductions in NO_x emission sup to 62 percent have been reported on a pulverized coal fired boiler when excess air is decreased from a level of 22 percent to a level of 5 percent.

Table 11–2

Possible NO_x emission reductions attainable with a 50% reduction in excess air from normal levels (greater than 10% excess air)

	Fuel Type		
	Gas	Oil	Coal
Furnace Type	% Reduction		
Horizontal front wall	15 – 20	20 – 25	25 – 35
Horizontal opposed firing	15 – 25	25 – 30	30 – 40
Tangentially fired	15	20 – 25	25 – 30

NOTE: Overall NO_x reduction potential for industrial and commercial size boilers for LEA operation is limited to about 40% reduction dependent upon the level of excess air normally applied.

(2) The successful application of LEA firing to any unit requires a combustion control system to regulate and monitor the exact proportioning of fuel and air. For pulverized coal fired boilers, this may mean the additional expense of installing uniform distribution systems for the coal and air mixture.

(3) Low excess air firing is a desirable method of reducing NO_x emission because it can also improve boiler efficiency by reducing the amount of heat lost up the stack. Consequently, a reduction in fuel combustion will sometimes accompany LEA firing.

d. Low excess air firing with load reduction. NO_x emissions may be reduced by implementing a load reduction while operating under low excess air conditions (table 11-2). This combined technique may be desirable in an installation where NO_x emissions are extremely high because of poor air distribution and the resultant inefficient operation of combustible equipment. A load reduction may permit more accurate control of the combustion equipment and allow reduction of excess air requirements to a minimum value. NO_x reduction achieved by simultaneous implementation of load reduction and LEA firing is slightly less than the combined estimated NO_x reduction achieved by separate implementation.

e. Two-stage combustion. The application of delayed fuel and air mixing in combustion boilers is referred to as two stage combustion. Two-stage combustion can be of two forms. Normally it entails operating burners fuel-rich (supplying only 90 to 95 percent of stoichiometric combustion air) at the burner throat, and admitting the additional air needed to complete combustion through ports (referred to as NO ports) located above and below the burner. There are no ports to direct streams of combustion air into the burner flame further out from the burner wall thus allowing a gradual burning of all fuel. Another form of two-stage combustion is off-stoichiometric firing. This technique involves firing some burners fuel-rich and others air-rich (high percentage of excess air), or air only, and is usually applied to boilers having three or more burner levels. Off-stoichiometric firing is accomplished by staggering the air-rich and fuel-rich burners in each of the burner levels. Various burner configuration tests have shown that it is generally more effective to operate most of the elevated burners air-rich or air only. Off-stoichiometric firing in pulverized coal fired boilers usually consists of using the upper burners on air only while operating the lower levels of burners fuel-rich. This technique is called overfire air operation.

(1) Two-stage combustion is effective in reducing NO_x emissions because: it lowers the concentration of oxygen and nitrogen in the primary combustion zone by fuel-rich firing; it lowers the attainable peak flame temperature by allowing for gradual

combustion of all the fuel; and it reduces the amount of time the fuel and air mixture is exposed to higher temperatures.

(2) The application of some form of two stage combustion implemented with overall low excess air operation is presently the most effective method of reducing NO_x emissions in utility boilers. Average NO_x reductions for this combustion modification technique in utility boilers are listed in table 11-3. However, it should be noted that this technique is not usually adaptable to small industrial boilers where only one level of burners is provided.

Table 11–3

Possible NO_x reductions, percent of normal emissions

	Fuel Type		
	Gas	Oil	Coal
Furnace Type	Percent Reduction		
Two-stage combustion			
Range	40 – 70	20 – 50	20 – 40
Average	50	40	35
Off-stoichiometric	—	—	39 – 60
Two-stage combustion or off-stoichiometric with LEA or load reduction			
Range	50 – 90	40 – 70	40 – 60
Average	70	60	50

f. Reduced preheat temperature. NO_x emissions are influenced by the effective peak temperature of the combustion process. Any modifications that lower peak temperature will lower NO_x emissions. Lower air preheat temperature has been demonstrated to be a factor in controlling NO_x emissions. However, reduced preheat temperature is not a practical approach to NO_x reduction because air preheat can only be varied in a narrow range without upsetting the thermal balance of the boiler. Elimination of air preheat might be expected to increase particulate emissions when burning coal or oil. Preheated air is also a necessary part of the coal pulverizer operation on coal fired units. Jn view of he penalties of reduced boiler efficiency and other disadvantages, reduced preheat is not a preferred means of lowering NO_x emissions.

g. Flue-gas recirculation. This technique is used to lower primary combustion temperature by recirculating part of the exhaust gases back into the boiler combustion air manifold. This dilution not only decreases peak combustion flame temperatures but also decreases the concentration of oxygen available for NO_x formation. NO_x reductions of 20 to 50 percent have been obtained on oil-fired utility boilers but as yet have not been demonstrated on coal-fired units. It is estimated that flue gas recirculation has a potential of decreasing NO_x emissions by 40 percent in coal-fired units.

(1) Flue gas recirculation has also produced a reduction on CO concentrations from normal operation because of increased fuel-air mixing accompanying the increased combustion air/ gas volume. Gas recirculation does not significantly reduce plant thermal efficiency but it can influence boiler operation. Radiation heat transfer is reduced in the furnace because of lower gas temperatures, and convective beat transfer is increased because of greater gas flow.

(2) The extent of the applicability of this modification remains to be investigated. The quantity of gas necessary to achieve the desired effect in different installations is important and can influence the feasibility of the application. Implementing flue-gas recirculation means providing duct work and recycle fans for diverting a portion of the exhaust flue-gas back to the combustion air windbox. It also requires enlarging the windbox and adding control dampers and instrumentation to automatically vary flue-gas recirculation as required for operating conditions and loads.

h. Steam or water injection. Steam and water injection has been used to decrease flame temperatures and reduce NO_x emissions. Water injection is preferred over steam because of its greater ability to reduce temperature. In gas and coal fired units equipped with standby oil firing with steam atomization, the atomizer offers a simple means for injection. Other installations require special equipment and a study to determine the proper point and degree of atomization. The use of water or steam injection may entail some undesirable operating conditions, such as decreased efficiency and increased corrosion. A NO_x reduction rate of up to 10 percent is possible before boiler efficiency is reduced to uneconomic levels. If the use of water injection requires installation of an injection pump and attendant piping, it is usually not a cost-effective means of reducing NO_x emissions.

11-4. Post combustion Systems for NO_x reduction.

a. Selective catalytic reduction (SCR) of NO_x is based on the preference of ammonia to react with NO, rather than with other flue-gas constitutents. Ammonia is injected so that it will mix with flue-gas between the economizer and the air heater. Reaction then occurs as this mix passes through a catalyst bed. Problems requiring resolution include impact of ammonia on downstream equipment, catalyst life, flue-gas monitoring, ammonia availability, and spent-catalyst disposal.

b. Selective noncatalytic reduction (SNR) Ammonia is injected into the flue-gas duct where the temperature favors the reaction of ammonia with NO_x in the flue-gas. The narrow temperature band which favors the reaction and the difficulty of controlling the temperature are the main drawbacks of this method.

c. Copper oxide is used as the acceptor for SO_2 removal, forming copper sulfate. Subsequently both the copper sulfate which was formed and the copper oxide catalyze the reduction of NO to nitrogen and water by reaction with ammonia. A regeneration step produces an SO_2 rich steam which can be used to manufacture by-products such as sulfuric acid.

11-5. Step-by-step NO_x reduction method

a. Applicability. The application of NO_x reduction techniques in stationary combustion boilers is not extensive. (However, NO_x reduction techniques have been extensively applied on automobiles.) These techniques have been confined to large industrial and utility boilers where they can be more easily implemented where NO_x emissions standards apply, and where equipment modifications are more economically justified. However some form of NO_x control is available for all fuel-burning boilers without sacrificing unit output or operating efficiency. Such controls may become more widespread as emission regulations are broadened to include all fuel-burning boilers.

b. Implementation. The ability to implement a particular combustion modification technique is dependent upon furnace design, size, and the degree of equipment operational control. In many cases, the cost of conversion to implement a modification such as flue-gas recirculation may not be economically justified. Therefore, the practical and economic aspects of boiler design and operational modifications must be ascertained before implementing a specific reduction technique.

(1) Temperature reduction through the use of two stage combustion and flue-gas recirculation is most applicable to high heat release boilers with a multiplicity of burners such as utility and large industrial boilers.

(2) Low excess air operation (LEA) coupled with flue-gas recirculation offers the most viable solution in smaller industrial and commercial size boilers. These units are normally designed for lower heat rates (furnace temperature) and generally operate on high levels of excess air (30 to 60%).

c. Compliance. When it has been ascertained that NO_x emissions must be reduced in order to comply with state and federal codes, a specific program should be designed to achieve the results desired. The program direction should include:

— an estimate of the NO_x reduction desired,
— selection of the technique or combination thereof, which will achieve this reduction;
— an economic evaluation of implementing each technique, including equipment costs, and changes in operational costs;
— required design changes to equipment
— the effects of each technique upon boiler performance and operational safety.

d. Procedure. A technical program for implementing a NO_x reduction program should proceed with the aid of equipment manufacturers and personnel who have had experience in implementing each of the NO_x reduction techniques that may be required in the following manner:

(1) NO_x *emission test.* A NO_x emission test should be performed during normal boiler load times to ascertain actual on-site NO_x generation. This test should include recording of normal boiler parameters such as: flame temperature; excess air; boiler loads; flue-gas temperatures; and firing rate. These parameters can be referred to as normal operating parameters during subsequent changes in operation.

(2) *Reduction capabilities.* The desired reduction in NO_x emissions, in order to comply with standards, should be estimated based on measured NO_x emission data. Specific NO_x reduction techniques can then be selected based on desired reductions and reduction capabilities outlined in preceding paragraph 11-3.

(3) *Equipment optimization.* Any realistic program for NO_x reduction should begin with an evaluation and overhaul of all combustion related equipment. A general improvement of boiler thermal efficiency and combustion efficiency will reduce the normal level of NO_x emissions. Of major importance are:

(a) the cleanliness of all heat transfer surfaces (especially those exposed to radiative heat absorption),
(b) maintaining proper fuel preparation (sizing, temperature, viscosity),
(c) insuring control and proper operation of combustion equipment (burners nozzles, air registers, fans, preheaters, etc.),
(d) maintaining equal distribution of fuel and air to all burners.

(4) *Low excess air operation.* Low excess air operation is the most recommended modific-ation for reducing NO_x emission. Possible reductions are given in preceding table 11-2. How-ever, a control system is needed to accurately monitor and correct air and fuel flow in response to steam demands. Of the control systems available, a system incorporating fuel and air metering with stack gas O_2 correction will provide the most accurate control. A system of this nature will generally pay for itself in fuel savings over a 2 to 3-year period, and is economically justified on industrial boilers rated as low as 40,000 lb of steam/hr.

(5) *Flue-gas recirculation.* Flue-gas recirculation is the second most effective NO_x reduction technique for boilers where two stage combustion cannot be applied. Low excess

air operation and flue-gas recirculation must be implemented simultaneously from a design point of view. LEA operation may require installation or retrofitting of air registers to maintain proper combustion air speed and mixing at reduced levels or air flow. Flue gas recirculation will require larger air registers to accommodate the increased volume of flow. Therefore, simultaneous application of LEA operation and flue-gas recirculation may minimize the need for redesign of burner air registers. Knowledge of furnace thermal design must accompany any application of flue-gas recirculation which effectively lowers furnace temperature and thus, radiative heat transfer. Convective heat transfer is also increased by increased gas flow due to the dilution of combustion air. It is advisable to consult boiler manufacturers as to the applicability of flue-gas recirculation to their furnaces.

e. Summary. The potential and applicability of each NO_x reduction technique is summarized in table 11-4.

TABLE 11-4

COMPARISON OF NO_x REDUCTION TECHNIQUES

Technique	Potential NO_x Reduction (%)	Advantages	Disadvantages
Load Reduction	See Figure 11-1	Easily implemented; no additional equipment required; reduced particulate and SO_x emissions.	Reduction in generating capacity; possible reduction in boiler thermal efficiency.
Low Excess Air Firing (LEA)	15 to 40 see Table 11-2	Increased boiler thermal efficiency; possible reduction in particulate emissions may be combined with a load reduction to obtain additional NO_x emission decrease; reduction in high temperature corrosion and ash deposition.	A combustion control system which closely monitors and controls fuel/air rations is required.
Two Stage Combustion			
Coal	30	-	Boiler windboxes must be designed for this application.
Oil	40	-	
Gas	50	-	Furnace corrosion and particulate emissions may increase.
Off-Stoichiometric Combustion			
Coal	45	-	Control of alternate fuel rich/ and fuel lean burners may be a problem during transient load conditions.
Reduced Combustion Air Preheat	10-50	-	Not applicable to coal or oil fired units; reduction in boiler thermal efficiency; increase in exit gas volume and temperature; reduction in boiler load.
Flue Gas Recirculation	20-50	Possible improvement in combustion efficiency and reduction in particulate emissions.	Boiler windbox must be modified to handle the additional gas volume; ductwork, fans and controls required.

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